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Investigation of Radical Intermediates in Polymer Sonochemistry

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Abstract

There is current interest in using high intensity ultrasound to perform a range of chemical transformations, including polymerisation reactions. Inthis work, the technique of radical trapping, primarily using DPPH, has been used to measure radical production rates in a range of monomer and related systems when exposed to high intensity ultrasound. It has been shown that realistic rates of production can be obtained around room temperature equivalent to thermal decomposition rates > 100 °C making sonication a viable method for initiating polymerisation. Rates of initiation in a two-phase organic in water system have also been measured. Some of the initiating species have been identified recording the esr spectra of adducts with spin traps although further analysis is needed before the complete range of radicals produced can be identified. The radicals arising from ultrasonic degradation of polymers have been studied using esr and it has been confirmed that radicals do not arise when heterolytic cleavage takes place.

Keywords: Sonochemistry; radical production; esr spectroscopy

Introduction

Sonication causes a range of chemical and physical effects in systems [1] . Applications in polymer science have been a rich area of exploitation of these effects both in synthesis and in the modification of existing polymers [2], [3] . A range of polymer synthesis methods have been shown to benefit from sonication [4], [5] .

It is widely accepted that most sonochemical effects can be attributed to cavitation [6] , the growth and explosive collapse of microscopic bubbles as a high energy sound wave propagates through the fluid. This can result in extreme conditions of temperature (> 2000K) and pressure (>500 bar) on a microsecond timescale [7] leading to the formation by 'sonolysis' of reactive intermediates such as radicals from breakdown of the solvent. A parallel reaction pathway exists for volatile solutes which can enter the bubble and be pyrollysed by the high temperatures. Physical effects are particularly important in multi-phase systems where the motion of fluid around the collapsing bubbles results in very efficient mixing, for example in forming emulsions, and the formation of jets of liquid onto suspended solids. An additional effect of importance in solutions containing polymers is that the rapid motion can result in effective shear degradation of polymer chains in the vicinity of cavitation bubbles [8] as long as they are over a certain molecular weight. The initial products of the chain breakage in organic polymers are two macromolecular radicals.

A large number of studies have been conducted into aqueous sonochemistry. The main species formed during sonication of water are H• and OH• radicals [9], [10] . These may recombine to form water, H_2 gas or H_2O_2. Alternatively, OH• radicals may react with volatile solutes that evaporate into the bubble during its growth or they may diffuse away and react with dissolved species in solution or at the bubble-solution interface. These radicals have been detected using spin-trapping techniques in conjunction with electron spin resonance, esr, spectroscopy [11], [12] and this has given valuable mechanistic information on a range of water based reactions. [13] The radical production has been exploited in the polymerisation of water soluble monomers such as acrylic acid or acrylamide. [14]

While cavitation is generally less efficient in common organic solvents, the production of radicals on sonication of organics was demonstrated some years ago. This process has also been used to make polymers by sonication of vinyl monomers such as styrene or methyl methacrylate, MMA. [15], [16] Conventionally, these polymerisations require the addition of thermally labile initiators such as peroxides or azo compounds. A major drawback in

sonochemical polymerisation of pure monomers is that only low conversions can be achieved since the increasing viscosity during the reaction inhibits cavitation. This does not apply in emulsion polymerisation where the organic monomer is dispersed in water. [17], [18] . This has been a fruitful area of study recently and it has been shown that polymerisation can take place in a simple dispersion of monomer in water without the need for added dispersants or initiators. [19], [20], [21] .

Sonochemistry is thus an area rich in radical reactions. In order to study these, a number of workers have made use of trapping reactive intermediates with the stable free radical 2,2-diphenylpicrylhydrazyl, DPPH. [22], [23], [24] . In previous work from this laboratory, DPPH trapping has been used to measure the rates of radical production in MMA polymerisation. [16] . DPPH is soluble in a wide range of organic solvents but not in water so that other traps have to be used for aqueous systems, an example being N-*t*-butyl-α-phenyl nitrone, TBPN [25] .

The aim of this paper is to extend previous measurements of the rates of sonochemical radical production to new systems and to consider the implications for ultrasound promoted polymerisations. Some attempts to identify the radicals using esr spectroscopy will also be described.

Experimental Details

Sonication techniques: Radical trapping experiments were performed using a Sonics and materials VC600 horn system operating at a fixed frequency of 23 kHz. The sound intensities used are reported below as appropriate and were measured calorimetrically in the usual way. The transducer produces mechanical vibrations which are coupled into the solution via a titanium horn as shown in Figure 1. Thermostatting was achieved to ± 0.5 °C by circulating water through a jacket surrounding the reaction vessel. [16] 100 cm^3 of the solution under study containing ~10^{-4} mol dm^{-3} DPPH in organic solvent or 5 x 10^{-4} mol dm^{-3} TBPN in water was pipetted into the reaction vessel and deoxygenated using nitrogen for thirty minutes at the appropriate temperature, simulating the conditions for a polymerisation. A small amount of solution was transferred to a spectrometer cell and tightly capped. After absorbance readings were taken, the solution was again deoxygenated before being returned to the reaction vessel to maintain a constant volume. For investigating a two-phase reaction, the vessel contained 90 cm^3 of the aqueous phase together with 10 cm^3 of a 10^{-4} mol dm^{-1} DPPH in σ-xylene. The system was deoxygenated as above. After sonication for the desired length of time, the

organic layer was recovered by 'breaking' the emulsion with 250 cm^3 of 30%w/v sodium chloride solution and recovering the separated organic layer. Here, the solution could not be returned to the flask; each experimental measurement was performed on a fresh sample.

Materials: Potassium persulphate (99+%), Azo-bisisobutyronitrile, AIBN (99%), Benzoyl peroxide (99%) and 2,2-diphenylpicrylhydrazyl, DPPH, (98%) were obtained from Aldrich and were used as received. The monomers and solvents used in the radical trapping experiments (Aldrich) were purified by passage through an inhibitor removal column and/or by distillation using standard procedures. Water was obtained from a Milli-Q_{plus} 185 system and had a resistance of > 10 MΩ. For esr spectroscopy, the radical traps *tert*-butyl phenyl nitrone, TBPN, and nitrosobenzene, NOB, were purchased from Sigma.

The polyisobutylene, PIB, used was obtained from Janssen Chemicals and the other polymers used were from Aldrich except poly(methyl phenyl silane) which was synthesised in our laboratories. [26]

Analytical methods: Ultra-violet/visible spectra were recorded in solution against a reference of pure solvent using a Perkin-Elmer PE330 spectrophotometer using cleaned quartz cells. Molar extinction coefficients for the solvents used were measured in the usual manner on solutions of accurately known concentrations. Electron Spin Resonance, esr, spectra were measured on a Bruker ESP300E spectrometer operating at 9.5 GHz which was calibrated with a DPPH signal. Sonication could not be carried out in the spectrometer cavity so that it was carried out on solutions containing spin traps. A Sonics and Materials VC50 was used to irradiate solutions under nitrogen for short periods before samples were removed into 5 mm o.d. silica tubes and spectra recorded as soon as possible after treatment.

Polymer molecular weights were measured on a Bruker LC21/41 Gel Permeation Chromatograph using tetrahydrofuran, THF, at a flow rate of 1 cm^3 min^{-1}. Calibration of the 60 cm 5 μm 'mixed' pore size column was performed with polystyrene standards. True molecular weights for PIB were obtained using a universal calibration procedure.

Results and Discussion

Rate of radical production in organic monomer systems

DPPH is commonly used in monitoring radical production. The vivid violet colour (λ_{max} = 520 nm,ε = 9.83 x 10^3 dm^3 mol^{-1} cm^{-1}) is gradually discharged on reaction with a radical

although it should be noted that the product $DPPH_2$ while pale orange in colour does have a small but significant absorption at 520 nm which must be accounted for.

The rate law for the reaction can be written as:

$$\text{Rate} = -\frac{d[DPPH]}{dt} = k[DPPH][R\bullet] = k[DPPH][CB] = k[DPPH]AI_{us}$$

where [R•] represents the concentration of radicals (of whatever identity) produced. This will be proportional to the concentration of cavitation bubbles, [CB] which in turn depends on the intensity, I_{us}, of the ultrasound used as well as the physical properties of the solvent. A is a term that simply collects the various proportionality constants together. Thus, at constant intensity:

$$-\frac{d[DPPH]}{dt} = k'[DPPH] \qquad (1)$$

so that first order kinetics would be expected. This has been observed by several authors although it should be noted that in many cases it is difficult to distinguish between zero and first order kinetics for the reactions.

In this work, we have found it difficult to obtain consistent results when monitoring polymerisations of monomers e.g. styrene. We have attributed this to interferences from other polymerisation routes and side reactions. It is also difficult to purify vinyl monomers to remove all traces of inhibitors or dissolved polymer. Thus, to estimate the initiation rates solely due to ultrasound, we have measured the rates of radical production in "cavitationally similar" solvents. The use of "model" solvents avoids these potential complications. There will be a degree of radical recombination and other side reactions but, since the radical must escape the primary solvent cage whether to initiate polymerisation or to react with the non-volatile DPPH, it is felt that the rate of trapping will closely mimic the rate of initiation. Cavitation in liquids is a complex phenomenon that depends on the ease of bubble formation, largely influenced by the density and surface tension and the strength of cavitational collapse, also influenced by these properties as well as the vapour pressure. We report here results on three monomers, styrene, methyl methacrylate, MMA, and α-methyl styrene for which we use as mimics σ-xylene, methylisobutyrate and cumene respectively. A comparison of the physical properties is given in Table 1.

Figure 2 shows typical results, plotted assuming first-order kinetics for the consumption of DPPH during sonication of σ-xylene under nitrogen gas at various temperatures. It is immediately noticeable that, contrary to most chemical reactions, the

process occurs faster at lower temperatures. This has been reported previously by a number of workers. [27], [28] Note that there is rather more scatter and uncertainty in the lower temperature results since it is more difficult to maintain a constant temperature. The major factor concerning the solution temperature that influences cavitation is the effect of the solution vapour pressure. At higher temperatures, there will be greater evaporation into the bubble. While it might be thought that this would provide higher levels of reactant which could breakdown to form radicals, it will "cushion" the collapse so that lower temperatures will be generated within the bubble. It will also serve to increase the thermal conductivity and polytropic ratio of the bubble contents, two additional factors which reduce the final temperature, T_{max} , reached on cavitational collapse.

Treating cavitation by a straightforward model in terms of an adiabatic collapse, T_{max} can be related [6], [29] to the ambient temperature and pressure, T_0 and P_a and the pressure in the bubble on collapse, P_v by:

$$T_{max} \approx T_0\left(\frac{P_a(\gamma'-1)}{P_v}\right) \qquad (2)$$

where γ' is the ratio of the heat capacities (c_p/c_v) of the gas/vapour inside the bubble. Thus, T_{max} and hence the rate of radical production from the solvent decreases as the temperature increases leading to the observed 'inverse' temperature dependence.

The rate constants calculated from this data are shown in Table 2. Comparison of these values with those for chemical initiators is instructive in terms of the anticipated rates of initiation in vinyl monomers. For example, the rate constant value for σ-xylene (and by analogy for styrene) at 25 °C is equivalent to that for the decomposition of AIBN at ~ 108 °C. Thus, simply by using ultrasound around room temperature, initiation rates comparable with those used in conventional methods can be achieved. Plotting the results in the Arrhenius format gave a linear relation with an 'apparent activation energy', E_a, of –7.5 kJ mol^{-1}.

Clearly the negative activation energies cannot be used to interpret the results in mechanistic terms. In an attempt to relate E_a to the radical production, Kruus [15] and Suslick [23] have replaced the ambient temperature in the Arrhenius equation by the temperature inside the cavitation bubble, T_{max}, leading to

$$\ln(k) = \ln(A) - \frac{E_a P_v}{RT_0 P_A(\gamma - 1)} \qquad (3)$$

where k is the observed rate constant. While there is a reasonable qualitative correlation with the solvent vapour pressure, extraction of E_A requires the value of P_A, the pressure in the bubble at collapse.

Using this equation and setting P_A to 1atm, a value for the activation energy is calculated to be 25.1 kJ mol^{-1}. However, the calculated activation energy is dependent upon the value for the acoustic pressure generated at the point of bubble collapse. It has been suggested that P_A [30] is likely to be an order of magnitude or more, higher. If P_A is set to 10 atm, then the activation energy increases to 250 kJ mol^{-1}. However, in the absence of knowledge of the precise conditions applying to cavitation bubbles, this approach is of limited quantitative use.

Lorimer and co-workers [24] have suggested that for solvents such as 1,2,4-trichlorobenzene, toluene and benzene, reaction of DPPH in the presence of ultrasound occurs by an abstraction reaction and not by reaction with radicals arising from cavitation bubble collapse. However, they were able to show a good correlation of results with the ultrasound intensity suggesting that cavitation did play a part. To investigate this further, we measured the rate of DPPH consumption in the absence of ultrasound. Reaction rates around ambient temperature were extremely slow so that measurements were made above 55 °C and extrapolated to lower temperatures. The measured activation energy, E_A, was 155 ± 15 kJ mol^{-1} for σ-xylene. This is somewhat higher than the 76 ± 8 kJ mol^{-1} found by Lorimer et al. using toluene but comparable with their result for 1,2,4-trichlorobenzene of 140 ± 20 kJ mol^{-1}. The measured rate constants are shown in Figure 3, the 'thermal' values at low temperatures being obtained by extrapolation.

It is clear that a reaction occurs even in the absence of ultrasound, presumably abstraction of hydrogen from the solvent. However, at temperatures below 35 °C, the rate is insignificant in comparison with that of the ultrasonic process. For example, at 25 °C, the abstraction rate is < 0.5% of the ultrasonic reaction. Thus around room temperature, DPPH trapping is a good measure of radical activity in these solvents.

To further investigate the use of ultrasound as an initiation method, the rate of reaction with DPPH was measured in solutions containing 0.1% by mass of two radical initiators, AIBN or BPO; the results for AIBN being shown in Figure 4. It can be seen from the rate constants, also listed in Table 2, that the rate of radical production is accelerated when solutions of these compounds are sonicated. For example, at 25 °C, DPPH is consumed some

3 - 4 times faster than when sonicating the σ-xylene alone. Again, any contribution from the thermal breakdown of the initiators may be considered negligible in comparison to the rates reported here. The rate constants for decomposition of AIBN and BPO at 25 °C are 2.7 x 10^{-6} min^{-1} and 7.37 x 10^{-7} min^{-1} respectively; less than 0.1% of the values measured here. Thus, sonication in solution appears to accelerate their decomposition by a factor in excess of 10^3.

With both of these initiators, the temperature dependence follows a more conventional relation, the rate of reaction increasing at higher temperatures. The Arrhenius plots are shown in Figure 5 and yield activation energies of 14.4 ± 1.9 kJ mol^{-1} and 25.58 ± 2.8 kJ mol^{-1} for AIBN and BPO respectively. These can be compared with the corresponding thermal decomposition values of 120 – 130 kJ mol^{-1} previously reported. [31], [32]

Of course, the rate constants shown in Table 2 are reported at the temperatures corresponding to the bulk solution in which the reaction is taking place. In a sonicated system, the temperature will not be homogeneous throughout the solution. There will be a thin shell of liquid around a bubble which will be warmed due to the heat generated during cavitation. In addition, after collapse, there will be a small region of solvent where this heat will be concentrated. If we consider the rate constants shown in Table 2 for 25 °C, these are equivalent to those expected for the thermal decomposition of the initiators at 120 – 130 °C. It must be emphasised that these are very much estimates which will depend on the particular system and conditions involved. They are not, for example, as precise as gas phase comparative thermometry [33] that has been used to give good estimates of the conditions pertaining inside cavitation bubbles. However, this may give some clue as to the approximate conditions that exist around cavitation bubbles in aromatic solvents such as σ-xylene.

These results are broadly in agreement with those obtained previously when studying methyl butyrate, a mimic for MMA [16] using a different sonication system and under different conditions. To illustrate this, Table 3 lists rate constants obtained at 25 °C for sonication of the pure solvent and when AIBN is added. The rate constant for MeOBu is lower than that for σ-xylene reflecting its higher vapour pressure [34] . Again the acceleration of AIBN decomposition was seen and, even in the absence of added initiator, the use of ultrasound gave radical production rates at 25 °C comparable to those obtained at > 70 °C under conventional conditions.

Also shown in Table 3 are results when using cumene as solvent. Cumene is an analogue for α-methyl styrene. Here, the rate of DPPH consumption is greater than with σ-

xylene since cumene has a lower vapour pressure. [34] The significance of these results lies in the fact that α-methyl styrene has a ceiling temperature of 61°C. This means that above this temperature, depolymerisation to monomer is favoured over polymerisation and so the polymer cannot be prepared by an addition mechanism [32] . When using the usual radical initiators such as AIBN or BPO the rates of radical production are too slow to be useful below 61°C. Thus, we were interested in the potential of using ultrasound to initiate polymerisation of this monomer around room temperature.

Despite numerous attempts under varying conditions, no polymerisation of α-methyl styrene could be achieved by sonication at low temperatures under conditions where styrene and MMA polymerised easily. The trapping experiments (including results obtained while sonicating the monomer in the presence of DPPH) confirm that radicals are being produced but no polymerisation resulted. The explanation may lie in the assumption that the bulk observable temperature represents the temperature of reaction in these systems. As outlined above, the areas around cavitation bubbles will be hotter and it may be that the radicals are formed but do not have a sufficiently long lifetime to diffuse far enough away from the bubble to reach a region of the liquid which is below 61°C. In contrast, the ceiling temperature of styrene is 235°C and for MMA is 165 °C so that the propagation is able to take place. It may be of significance that an attempt to produce poly(α-methyl styrene) by sonication while suspended in an ultrasonic cleaning bath rather than a horn system did produce a small amount of polymer. Here, the cavitation would be less violent and so there may be an effect of the sound intensity affecting the maximum bubble size and hence the maximum temperature generated on collapse. This effect is under further study.

Rate of radical production in aqueous systems.

In related work [25] we have used a similar technique in aqueous solutions by following the decolourisation of TBPN (λ_{max} = 285 nm). Table 4 shows the rate constants recorded for 1 g dm^{-3} solutions of potassium persulfate; this concentration being typical of that used for initiation of aqueous polymerisation.

The Arrhenius plot of the data recorded in the absence of ultrasound yielded an activation energy of 121 ± 12 kJ mol^{-1}. In this case the temperature dependence of the sonochemical is more conventional in that the rate increases with rising temperature. An Arrhenius plot of the results recorded in the presence of ultrasound showed distinct curvature.

This is due to the relatively larger contribution made by the 'silent' process i.e. in the absence of ultrasound. In contrast to AIBN or BPO, the decomposition of persulfate occurs at a measurable rate even at 25 °C. The 'ultrasonic' rate for this system is equivalent to that obtained at 55 °C under conventional conditions.

Rate of radical production in heterogeneous systems.

An emulsion polymerisation is a complex system of reactions [17] . Radical production usually occurs in the aqueous phase via a redox initiator such as a persulfate salt. The monomer exists as large droplets which serve as a reservoir while the polymerisation proceeds in monomer swollen micelles formed from the added surfactant. Thus, radicals have to diffuse from the aqueous phase into the micelles to start the reaction.

As far as we are aware, radical trapping in sonochemical systems has previously only been carried out in single phase systems. Given the recent interest in sonochemical heterophase reactions such as emulsion polymerisation, we were interested to determine if these techniques could yield valuable information here. To simplify the situation, we have simply used a mixture of σ-xylene (containing DPPH) and water in the ratio 10:90, omitting the surfactant. It was not possible to perform experiments when surfactant was included in the mixture since the emulsion was too stable and the organic phase could not be recovered.

The σ-xylene : water mixture readily forms a suspension in which the organic droplet size will be in the region of 0.5 – 5 μm [35] . Thus, they are smaller than a cavitation bubble (although the bubbles reach these dimensions at the final stages of collapse) and hence the main site of cavitation will remain the aqueous phase. Since DPPH is insoluble in water, this technique should give a good indication of the rate at which radicals are able to enter the organic phase after being formed in the aqueous phase. Attempts were made to measure radical concentrations in the aqueous phase but this was not possible since even after prolonged settling it remained cloudy preventing use of optical spectroscopy.

Figure 6 shows the first order plot of DPPH consumption when sonicated in the σ-xylene / water mixture at 25 °C. It can be seen that a significant concentration of DPPH reacts despite it being inaccessible to the primary radicals arising from cavitation. Diffusion of radicals from the aqueous phase into the σ-xylene must therefore occur although it is not clear whether these are the hydroxyl radicals initially formed or the product of subsequent reactions. Also shown In Figure 6 are the results when potassium persulfate is added to the aqueous

phase. This increases the rate of radical reaction by up to ten-fold. The rate constants measured over a range of temperatures are listed in Table 5. Arrhenius plots of the data were prepared and demonstrated reasonably linear correlations. However, given the nature of the system in terms of aqueous cavitation and the effect that the suspended organic solvent would have as well as the various diffusion and phase transfer processes that occur before the radicals can react with DPPH, interpretation of any activation energy is fraught with difficulty and uncertainty. The radical concentrations produced are comparable with those in the wholly organic system demonstrating the utility of low temperature sonication as a method of initiating heterophase polymerisation. As far as we are aware, these are the first reported measurements of radical production rates in a two-phase system. The implications of the measured rates for sonochemical polymerisation will be discussed in a forthcoming publication [36] .

Esr study of radical intermediates

Having established that satisfactory rates of radical production could be obtained by sonication, esr spectroscopy was used to obtain information on the identity of the radical species. It should be noted that it was not possible to conduct sonications *in-situ* in the spectrometer cavity. The radicals produced have a short lifetime so that *ex-situ* production was not feasible. Thus, a spin trapping method was adopted. The drawback here is that the primary spectral information is given by the trap so that only limited structural information can be obtained.

Two spin traps were used, TBPN and nitrosobenzene, NOB. The structures of the traps and the presumed radical adducts are shown in Figure 7. The unpaired electron will couple with the nitrogen (nuclear spin, I = 1) giving rise to a three line spectrum. Further coupling with magnetically active nuclei (such as hydrogen) will split these peaks.

The esr spectrum of the reaction product from sonication for 5 min of AIBN in methyl butyrate containing TBPN is shown in Figure 8. The expected three-line spectrum is observed. However, no further information could be deduced since, as shown above the major proportion of the radicals will be those arising from breakdown of AIBN. Differentiation of the spectrum showed a small splitting of each peak due to the hydrogen on the carbon adjacent to the nitrogen but the cyanopropyl radicals will give adducts with hydrogen atoms too far away from the radical centre to give further coupling.

Sonication of MMA in the presence of TBPN but with no added initiator gave the spectrum in Figure 9(a). The spectral intensity is lower than in Figure 8 indicating a lower concentration of radicals formed in the same reaction time. This correlates well with the DPPH trapping results described above although the experimental conditions are different. The spectrum is more complex. The basic three-line spectrum is split by the α-hydrogen but additional splittings are evident. Analysis of the spectrum showed multiple splittings which could not be fitted on a simple model. The best fit to the data came from assuming that the radical centre was coupling to a mixture of hydrogen atoms and methyl or other alkyl fragments. However, no quantitative information could be determined and it is clear that the intermediates arising from sonication comprise several species. It is however, noteworthy that when MMA-d_3 was used with the ester methyl deuterated, the spectrum was dignificantly modified, as shown in Figure 9(b). Thus, it is clear that radicals arising from this methyl group are formed. Further work is needed before a precise assignment of the radicals can be made.

Radical production in polymer systems

The cleavage of polymer chains when irradiated with ultrasound in solution leading to a reduction in the polymer molecular weight is one of the earliest reported sonochemical phenomena [8] . The chains are stretched out in the solvent flows around the collapsing bubbles and sufficient strain can be induced to break bonds in the chain. The primary product in carbon backbone polymers is a pair of macromolecular radicals arising from homolytic bond breakage. The radicals can be used as a reactant to prepare functionalised polymers. However, there remain questions as to the identity of the intermediates such as whether branching and rearrangement can occur at the radical chain ends.

The presence of radical intermediates is confirmed by the esr spectra, shown in Figure 10, of sonicated solutions (1% in tetrahydrofuran) of poly(isobutylene), PIB, trapped with nitrosobenzene. To maximise the chain breakage relative to solvent breakdown, a low ultrasound intensity (10 W cm^{-2}) was used. The spin trap gives rise to the main triplet seen in the spectrum but the further splitting seen in the second differential spectrum (see inset in Figure 10) is consistent with the CH_2• radical produced on cleavage of a PIB chain as illustrated in Figure 11. The other radical has no primary hydrogens and hence causes no splitting.

To investigate the efficiency of trapping, separate experiments were performed by sonication of PIB under the same conditions as above with an excess concentration of DPPH. The consumption of DPPH ($\varepsilon_{520\ nm}$ = 970 $m^2\ mol^{-1}$) during sonication is shown in Figure 12. The rate constant for DPPH consumption (and hence radical production) in THF alone was 0.0090 min^{-1} while this increased to 0.0287 min^{-1} when PIB was present, the difference being taken as the rate of production of radicals at polymer chain ends. GPC analysis showed that the number average molecular weight of the polymer fell from 1.27 x 10^6 to 2.34 x 10^5 giving an average of 4.43 chain breaks.

Comparing the rate of DPPH consumption with the number of chain breaks indicates a trapping efficiency of (96 ± 5) %, the major error arising from the accuracy with which GPC can measure the molecular weights. However, this high value indicates that we obtain essentially quantitative trapping of the macromolecular radicals.

The esr spectra recorded during ultrasonic degradation of poly(methyl methacrylate), PMMA, were similar to those for PIB since this will also give rise to —CH_2• and —RR'C• radicals. That for polystyrene, illustrated in Figure 13 differs since both macroradicals will carry hydrogens which will split the nitrogen triplet. The resulting spectrum is consistent with the superposition of the spectra arising from the two radical species shown in Figure 14.

While the sonochemistry of organic polymers is reasonably well understood, there has been recent interest in the production of inorganic backbone materials such as siloxanes, silanes and phosphazenes. [37] It was suggested some years ago [38] that sonication of siloxanes which have an alternating silicon – oxygen backbone gave rise not to radical species but to an ion pair due to heterolytic fission of the Si — O bond. We attempted radical trapping experiments using poly(dimethyl siloxane) but found no decolourisation of DPPH in excess of that expected from the solvent. As shown in Figure 15, no esr signal was detected although it is known that chain breakage occurs. [39] Both these experiments confirm that this polymer does not form radicals and we are currently performing nmr experiments to investigate the ion-pair hypothesis. To confirm that this was not simply an artefact of having silicon in the chain, poly(methyl phenyl silane) which has an all silicon backbone was degraded and gave the esr spectrum in Figure 16. The basic three peak spectrum due to radical species on nitrogen is clearly seen so that we conclude that homolytic bond braekage also occurs in this material. The additional structure in the spectrum is due coupling of the small amount of magnetically active silicon nuclei (^{29}Si, I = ½, abundance = 4.1%).

Conclusions

The technique of DPPH trapping has been used to measure radical production rates in a range of monomer and related systems when exposed to high intensity ultrasound. It has been shown that realistic rates of production can be obtained around room temperature equivalent to thermal decomposition rates > 100 °C making sonication a viable method for initiating polymerisation. Rates of initiation in a two-phase organic in water system have also been measured. Although further analysis is needed, some progress has been made in identifying the radicals produced on sonication of these compounds by recording the esr spectra of adducts with spin traps.

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Table 1. Physical properties of vinyl monomers and their 'cavitational mimics' [34]

Property	σ-xylene	Styrene	Methyl butyrate	MMA	Cumene	α-methyl styrene
Molecular weight	106.17	104.15	102.12	100.13	120.20	118.18
Boiling point / °C	144.4	145.2	102.3	100.5	153.0	165.5
Density / g cm^{-3}*	0.8802	0.9060	0.8984	0.944	0.864	0.9046
Vapour Pressure / torr *	6.6	6.4	32.5	38.5	4.5	1.9

* property at 25 °C

Table 2. Rate constants (10^3 min^{-1}) for the sonication of DPPH in σ-xylene at an intensity of 23.8 ±0.5 Wcm^{-2}.

Temperature /°C	σ-xylene	σ-xylene + AIBN	σ-xylene + BPO
-5	3.50	2.70	7.60
10	2.70	4.30	
25	2.45	7.8	11.3
35	2.35	9.30	13.9
45	2.01	13.4	18.7
55	1.80	24.9	22.1

Table 3. Rate constants (10^3 min^{-1}) for DPPH consumption at 25 °C and sonication intensity of 33.1 ±0.53 Wcm^{-3}.

	solvent	**Solvent + 0.1% AIBN**
σ-xylene	3.1	10.9
Methyl butyrate	1.03	3.12
Cumene	6.1	13.1

Table 4. Rate constants (10^3 min^{-1}) for sonochemical reaction of potassium persulfate in water at an intensity of 16.2 W cm^{-2}

Temperature / °C	**Thermal**	**Sonochemical**
25	0.012	0.05
35	0.07	0.07
45	0.25	1.09
55	0.59	1.67
65	4.37	4.18

Table 5. Rate constants (10^3 min^{-1}) for consumption of DPPH in σ-xylene /water mixtures

Temperature / °C (± 0.5)	**σ-xylene /water**	**σ-xylene /water + 0.5% $K_2S_2O_8$**
2	0.381	3.93
25	0.485	4.46
35	0.636	4.82
45	0.661	5.41
55	0.657	7.12

Captions for Figures

Figure 1. Schematic diagram of sonication apparatus

Figure 2. First order rate plot for DPPH consumption during sonication of σ-xylene at 23.8 ±0.5 Wcm^{-2} and the indicated temperatures (°C).

Figure 3. Comparison of sonochemical and thermal rate constants for DPPH consumption in σ-xylene at 23.8 ±0.5 Wcm^{-2} and 25 °C.

Figure 4. First order rate plot for DPPH consumption during sonication of AIBN in σ-xylene at 23.8 ±0.5 Wcm^{-2} and the indicated temperatures (°C).

Figure 5. Arrhenius plots for DPPH consumption in σ-xylene containing azobis-isobutyronitrile (AIBN) or benzoyl peroxide (BPO) at 23.8 ±0.5 Wcm^{-2}.

Figure 6. First order rate plot for TBPN consumption during sonication of water with the indicated amounts of potassium persulfate.

Figure 7. Structures of spin traps and radical adducts

Figure 8. Electron spin resonance spectra of trapped radicals from sonicated AIBN in MMA

Figure 9. Electron spin resonance spectra of trapped radicals from sonicated (a) MMA and (b) d_3-MMA.

Figure 10. Electron spin resonance spectra of trapped radicals from sonicated AIBN in MMA

Figure 11. Electron spin resonance spectra of trapped radicals from sonicated poly(isobutylene) in THF. The inset shows the differential spectrum.

Figure 12. DPPH consumption during sonication of THF and 1% poly(isobutylene) in THF

Figure 13. Electron spin resonance spectra of trapped radicals from sonicated polystyrene in THF

Figure 14. Radical formation on chain cleavage for polystyrene

Figure 15. Electron spin resonance spectra of sonicated poly(dimethyl siloxane) in THF

Figure 16. Electron spin resonance spectra of trapped radicals from sonicated poly(methyl phenyl silane) in THF

Fig. 1

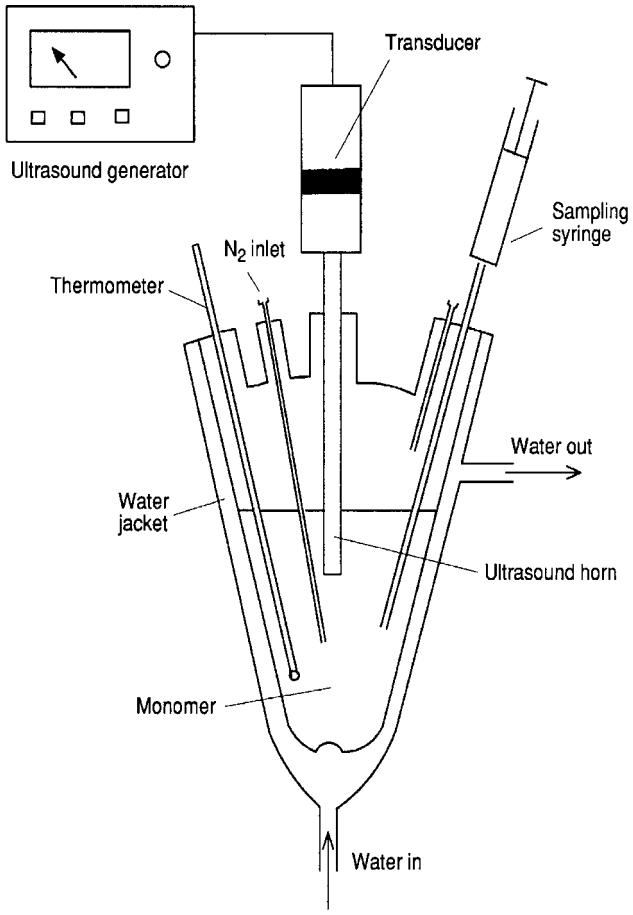

Transducer
Ultrasound generator
Sampling syringe
N_2 inlet
Thermometer
Water out
Water jacket
Ultrasound horn
Monomer
Water in

Fig. 2

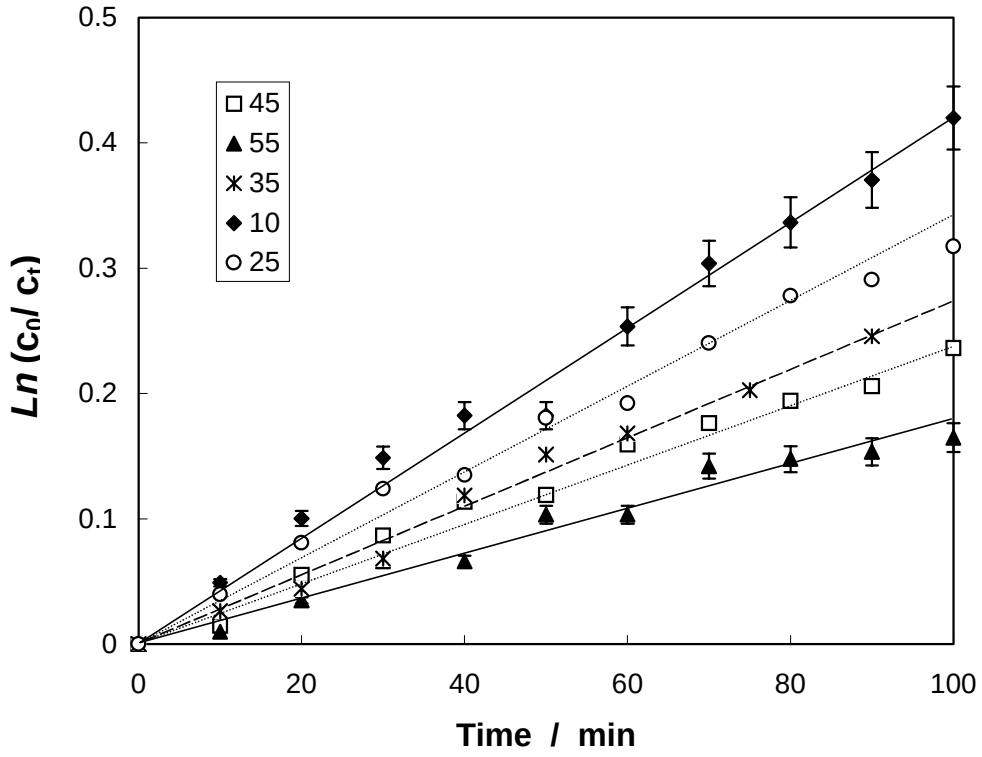


Fig. 3

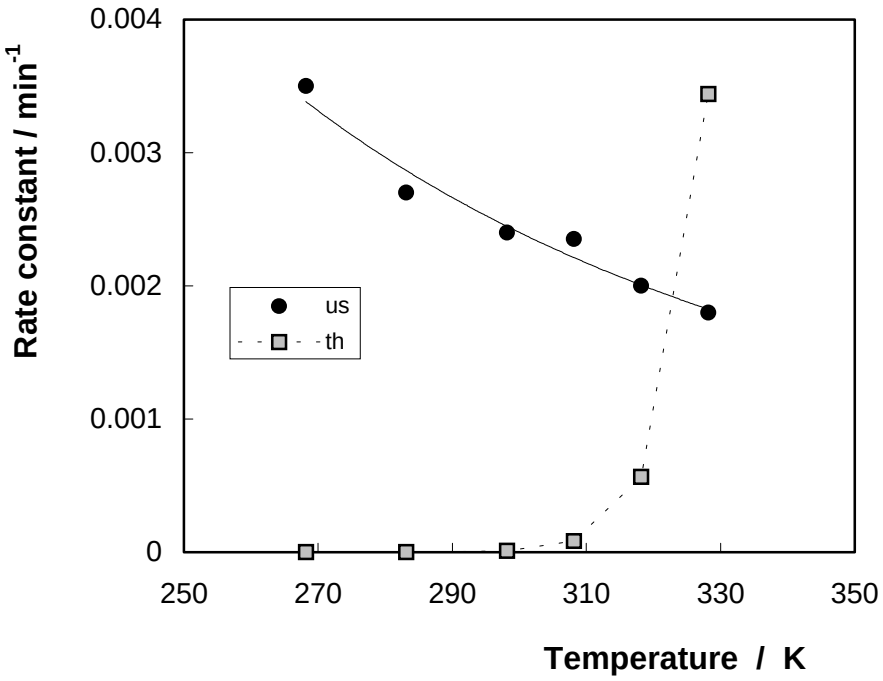

0.004
0.003
0.002
0.001
0
Rate constant / min-1
us
th
250
270
290
310
330
350
Temperature / K

Fig. 4

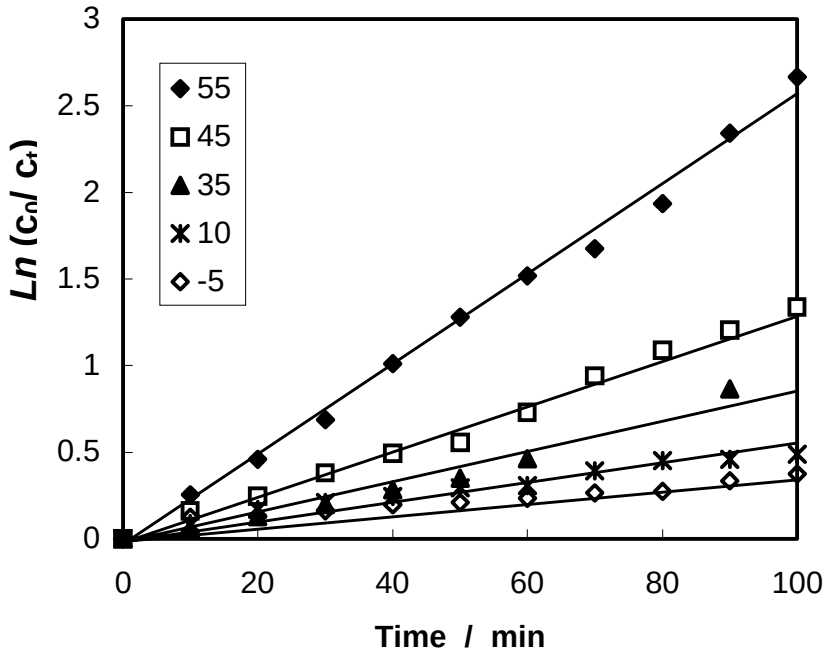


Fig. 5

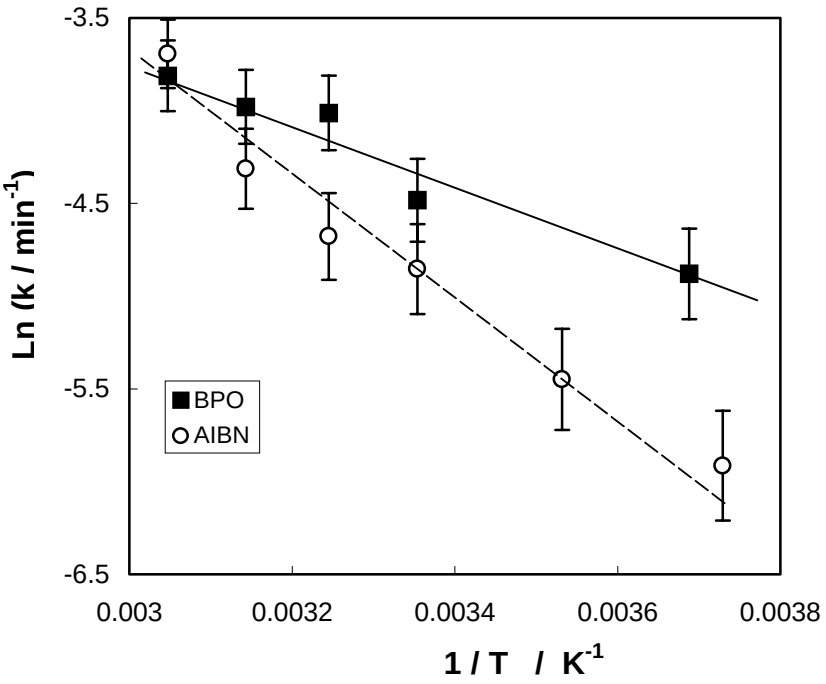

-3.5
-4.5
-5.5
-6.5
Ln (k / min-1)
BPO
AIBN
0.003
0.0032
0.0034
0.0036
0.0038
1 / T / K-1

Fig. 6

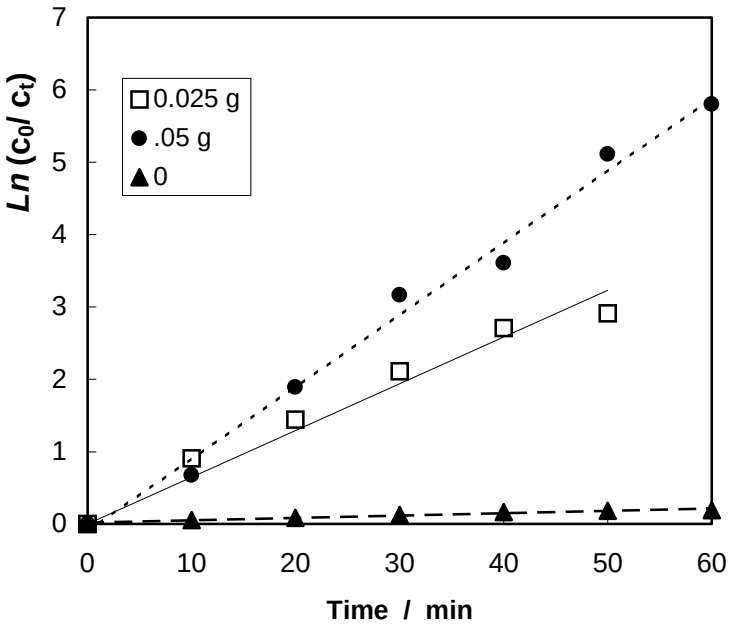


Fig. 7

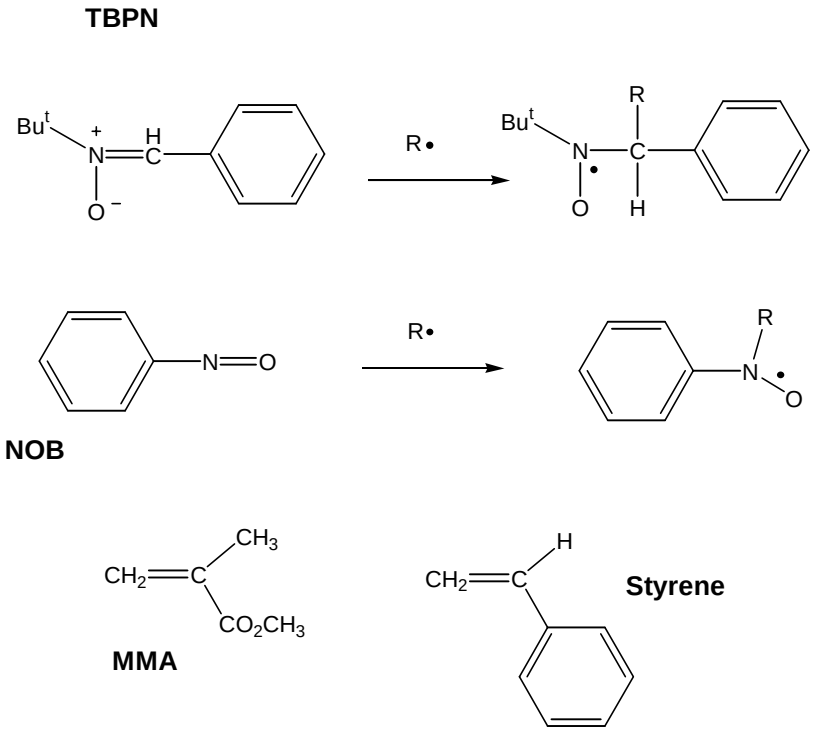

TBPN
Bu t
+
N
H
C
O −
R•
R
Bu t
N
C
O
H
N O
R•
R
N
O
NOB
CH3
CH2
C
CO2CH3
MMA
H
CH2
C
Styrene

Fig. 8

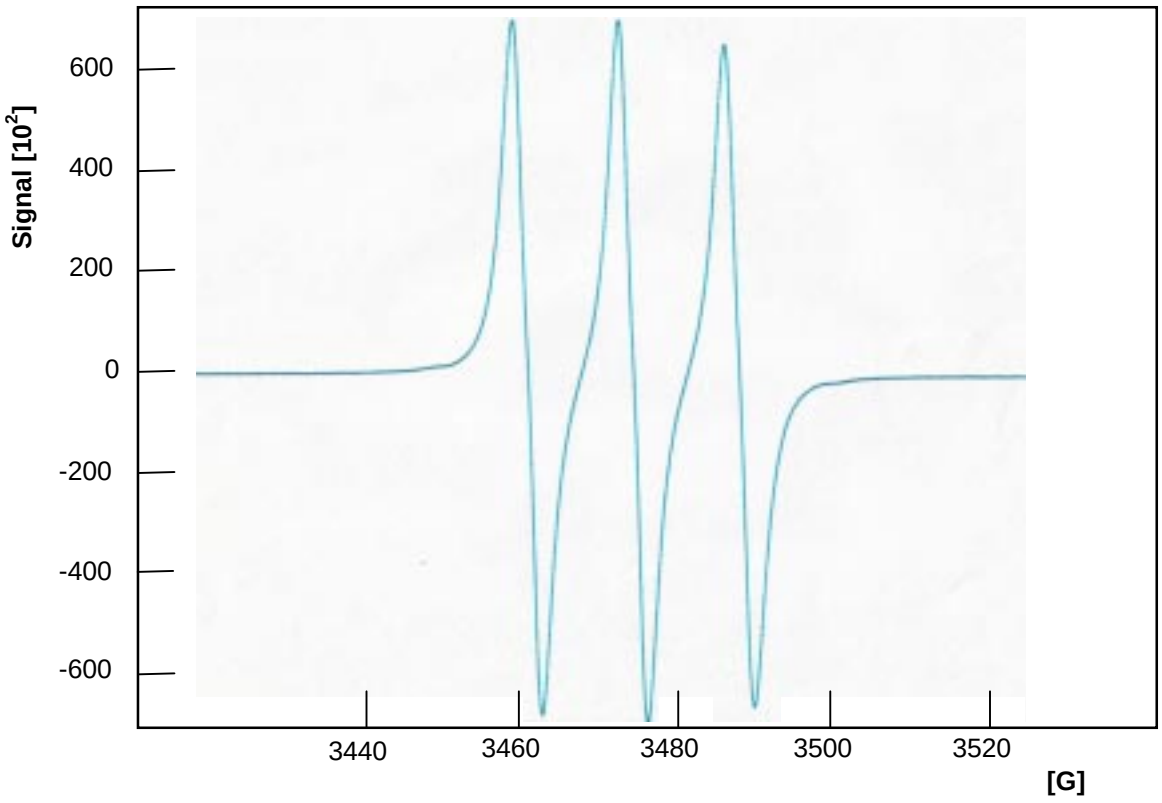


Fig. 9

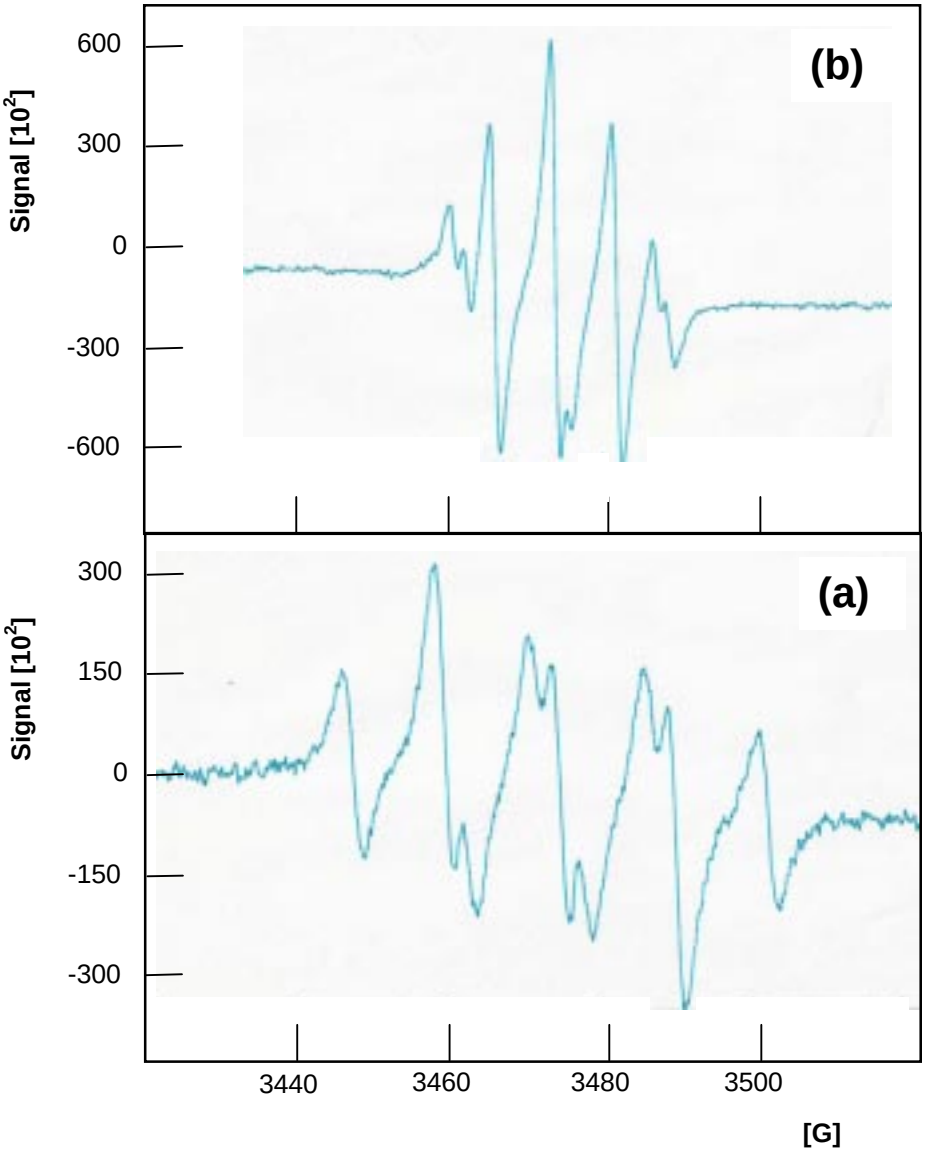


Fig. 10.

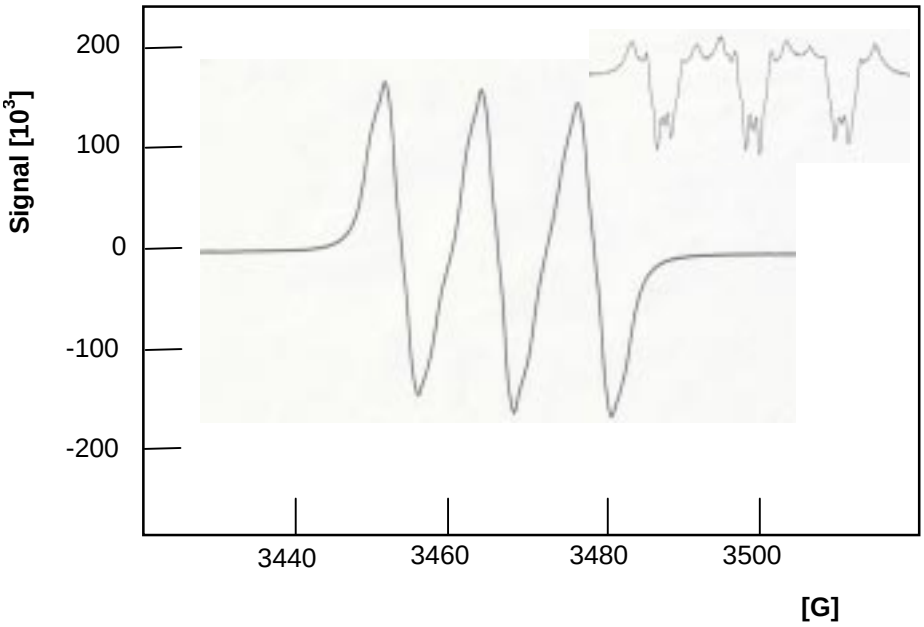


Fig. 11

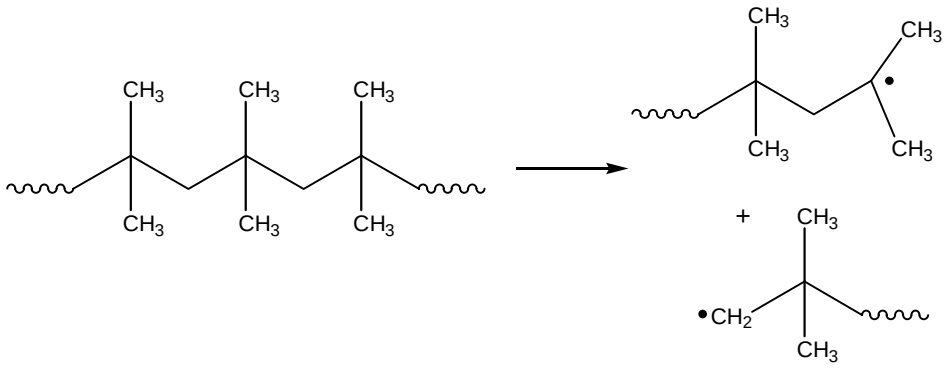


Fig. 12

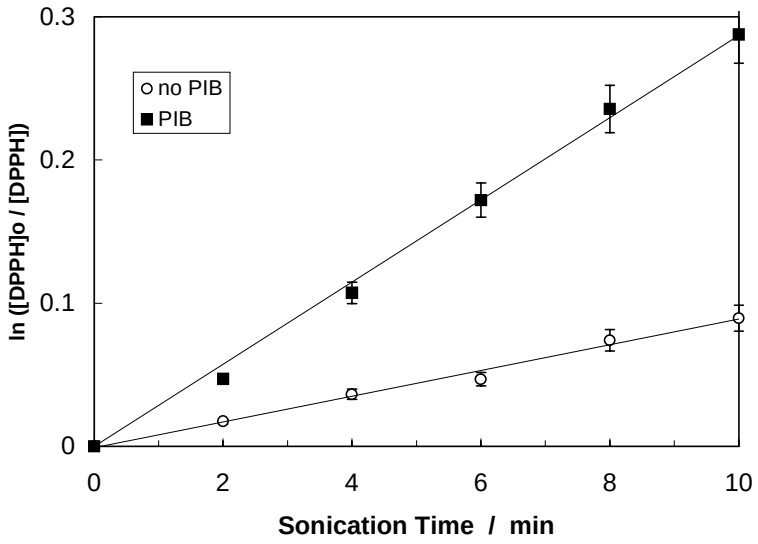

0.3
0.2
0.1
0
0
2
4
6
8
10
ln ([DPPH]o / [DPPH])
Sonication Time / min
no PIB
PIB

Fig. 13

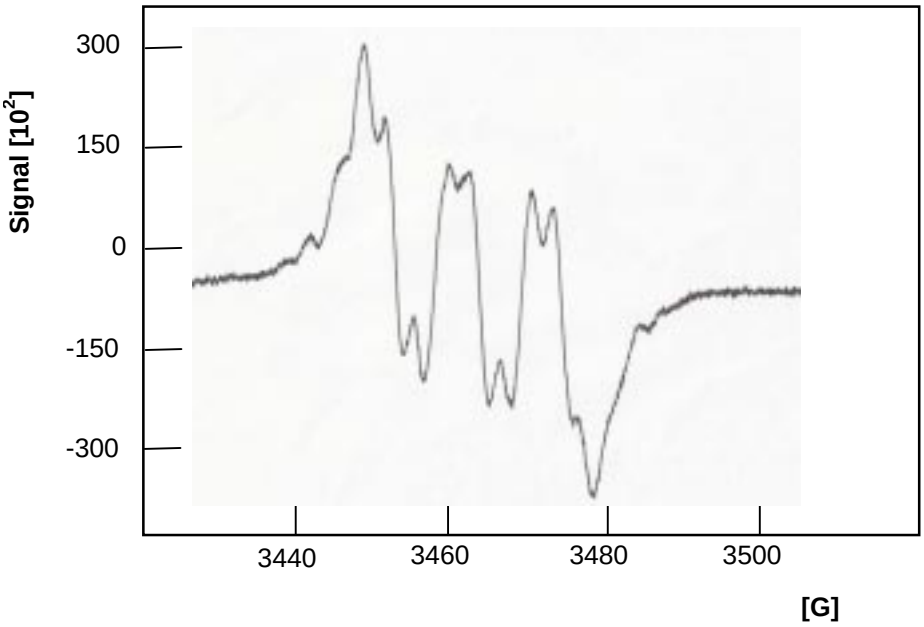


Fig. 14

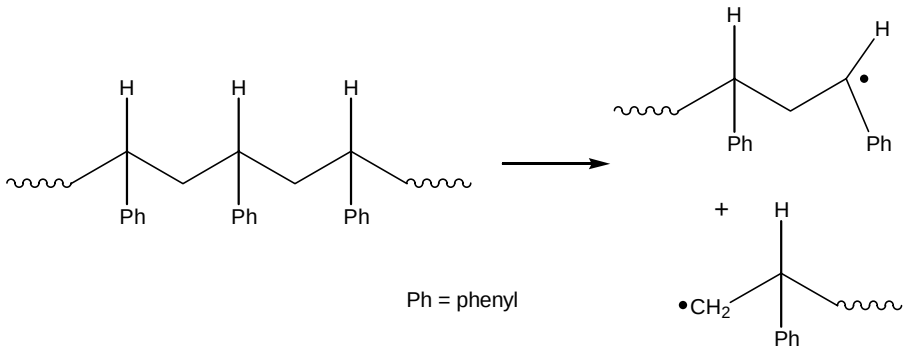
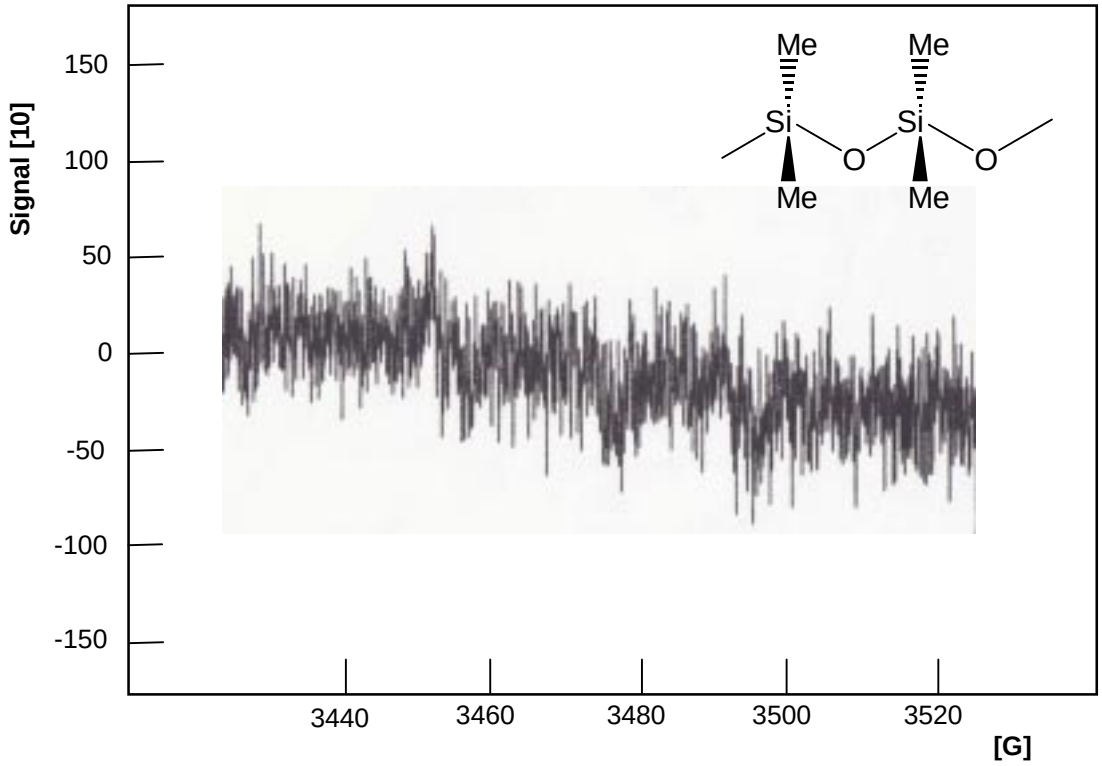


Fig. 15.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100
50
0
-50
-100
-150
3440
3460
3480
3500
3520
[G]
Me
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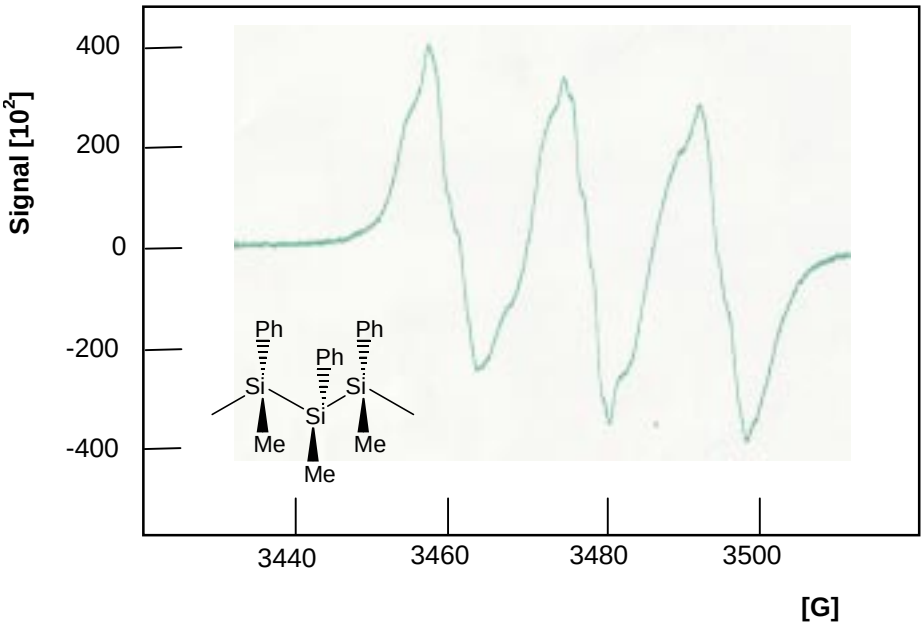
Si
Si
O
O
Me
Me

Fig. 16.


Signal [10²]
400
200
0
-200
-400
Ph
Ph
Ph
Si
Si
Si
Me
Me
Me
3440
3460
3480
3500
[G]